

AD-A094 029

GENERAL ELECTRIC CO PHILADELPHIA PA  
IMPROVED CERAMIC HEAT EXCHANGER MATERIALS.(U)  
DEC 80 H W RAUCH, L R MCCREIGHT

F/G 11/2

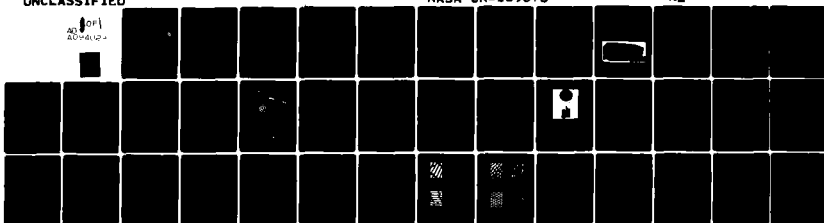
UNCLASSIFIED

NASA-CR-159678

NAS3-19698

NL

AD  
20-44-12-1



END  
DATE  
FILMED  
12-84  
DTIC

150  
**LEVEL**

①

DOE/NASA/9698-2  
NASA CR-159678

## **IMPROVED CERAMIC HEAT EXCHANGER MATERIAL**

**AD A094029**

H.W. Rauch, Sr., & L.R. McCreight  
GENERAL ELECTRIC COMPANY  
Philadelphia, Pennsylvania

**DTIC  
COLLECTED  
JAN 23 1981**  
C

**DECEMBER 1980**

Prepared for the  
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
Lewis Research Center  
Cleveland, Ohio 44135

Contract NAS 3-19698

**DISTRIBUTION STATEMENT A**

Approved for public release;  
Distribution Unlimited

**DDC FILE COPY**

As a part of the  
**DEPARTMENT OF ENERGY**  
Division of Transportation Energy Conservation  
Heat Engine Highway Vehicle Systems Program

**80 21 087**

#### NOTICE

This report was prepared to document work sponsored by the United States Government. Neither the United States nor its agent, the United States Energy Research and Development Administration, nor any Federal employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

7. Final

1

1. Report No. NASA CR-159678		2. Government Accession No. AD-A094029		3. Recipient's Catalog No.	
4. Title and Subtitle IMPROVED CERAMIC HEAT EXCHANGER MATERIALS.				5. Report Date December 1980	
				6. Performing Organization Code	
7. Author(s) Harry W. Rauch, Sr. and Louis R. McCreight				8. Performing Organization Report No. 1411	
9. Performing Organization Name and Address General Electric Company Advanced Energy Programs Department P.O. Box 8555 Philadelphia, Pa. 19101				10. Work Unit No.	
12. Sponsoring Agency Name and Address Department of Energy Division of Transportation Energy Conservation Washington, D.C. 20545				11. Contract or Grant No. NAS 3-19698 new	
				13. Type of Report and Period Covered Contractor Report	
				14. Sponsoring Agency Code DOE/NASA/9698-2	
15. Supplementary Notes Final Report. Prepared under Interagency Agreement EC-77-A-31-1011 Project Manager, Dr. Thomas P. Herbell, Materials Division, NASA Lewis Research Center, Cleveland Ohio 44135					
16. Abstract <p>Numerous compositions were developed and evaluated for potential application as heat exchanger structures in automotive gas turbine engines. Test specimens in the form of small monolithic bars were evaluated for thermal expansion and dimensional stability before and after exposure to sea salt and sulfuric acid, followed by short and long term cycling at temperatures up to 1200°C (2192°F). Materials which survived the screening tests were considered for fabrication into honeycomb form. The material finally selected, GE-7808, consists of the oxides, <math>ZrO_2</math>-<math>MgO</math>-<math>Al_2O_3</math>-<math>SiO_2</math>, and is described generically as ZrMAS. The original version on which the primary work was done was based on a commercially available cordierite (MAS) frit. Late in the program, however a clay/talc mixture was demonstrated to be a satisfactory very low cost source of the cordierite (MAS) phase.</p> <p>Several full size honeycomb regenerator cores, about 10.2 cm thick and 55 cm diameter (4" x 22") were fabricated by Coors Porcelain Company from both the frit and mineral versions of GE-7808. The honeycomb cells in these cores had rectangular dimensions of about 0.5 mm x 2.5 mm (0.02" x 0.1") and a wall thickness of approximately 0.1 mm (0.004"). Test specimens cut from the cores were evaluated both in our laboratory and at the Ford Motor Company.</p> <p>This program also included a brief effort to improve a lithium aluminosilicate (LAS) material which has developed under this contract several years ago. However, the recognized susceptibility of lithium containing materials to acid attack prompted discontinuation of this work.</p> <p>A major benefit of the multi-phase materials developed in this program was demonstrated during the fabrication and firing operations of the honeycomb structure. Their refractoriness and rheological behavior enabled them to retain shape and orientation of the gas passages parallel to the axis much better than some single phase (glass ceramic) materials.</p> <p>The test data show that GE-7808 is significantly more stable at 1100°C (2012°F) in the presence of sodium than the Corning 9460 aluminosilicate reference materials. In addition, thermal exposure up to 1100°C, with and without sodium present, results in essentially no change in thermal expansion of GE-7808.</p> <p>Overall assessment of GE-7808 properties, ease of material preparation, noncritical materials utilized and ready adaptability to honeycomb fabrication qualify this new material as a candidate for heat exchanger applications in automotive gas turbine engines.</p>					
17. Key Words (Suggested by Author(s)) Ceramic Honeycomb Heat Exchanger Low expansion ceramics Chemically stable ceramics			18. Distribution Statement  Unclassified - Unlimited		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages A03	
				22. Price*	

For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA CR-159678-10

DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution Unlimited

JAN 23 1981

## TABLE OF CONTENTS

Section		Page
1	FOREWORD . . . . .	1
2	SUMMARY . . . . .	2
3	INTRODUCTION . . . . .	9
4	MATERIALS DEVELOPMENT . . . . .	12
5	MATERIALS EVALUATIONS AND RESULTS. . . . .	14
	5.1 Thermal Phase Stability . . . . .	14
	5.2 Thermal Expansion . . . . .	16
	5.3 Corrosion Resistance . . . . .	20
	5.4 Acid Testing . . . . .	20
	5.5 Salt Testing . . . . .	20
	5.6 Dimensional Stability . . . . .	21
	5.7 Mechanical Properties . . . . .	25
	5.8 Ford Motor Company Tests . . . . .	25
	5.9 Microstructure and Related Properties . . . . .	26
6	DISCUSSION OF RESULTS . . . . .	30
7	COST STUDY . . . . .	32
8	CONCLUSIONS . . . . .	33
9	REFERENCES. . . . .	34

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

# LIST OF ILLUSTRATIONS

Figure		Page
1	Cross Section of GE-7808 Regenerator Core . . . . .	3
2	Thermal Expansion of GE-7808 . . . . .	7
3	Thermal Expansion of GE-7808 . . . . .	7
4	Dimensional Stability of GE-7808 and Corning-9460 . . . . .	8
5	Typical Coated Paper Wrapping Operation . . . . .	10
6	Typical Embossing Operation . . . . .	11
7	Typical Extrusion Operation . . . . .	11
8	Effect of Thermal Cycling During Phase Stability Study on Dimensional Stability . . . . .	15
9	Measuring Device . . . . .	16
10	Thermal Expansion of GE-3202 vs. Temperature . . . . .	18
11	Effect of Firing Temperature on the Corrosion Resistance of GE-3202 as Indicated by Thermal Expansion . . . . .	18
12	Thermal Expansion of GE-3202 and Corning 9460 . . . . .	18
13	Thermal Exposure of Corrosion Tested GE-7808 . . . . .	18
14	Effect of Firing Temperature on Thermal Expansion of GE-7808 . . . . .	19
15	Effect of Corrosion Testing on Thermal Expansion of GE-7808 . . . . .	19
16	Thermal Expansion of Several Candidate Heat Exchanger Materials . . . . .	19
17	Effect of Acid Treatment on Dimensional Stability of GE-3202 . . . . .	22
18	Effect of Salt Treatment on Dimensional Stability of GE-3202 . . . . .	22
19	Effect of Acid Treatment on Dimensional Stability of GE-7808 . . . . .	22
20	Effect of Salt Treatment on Dimensional Stability of GE-7808 . . . . .	22
21	Effect of Long Term Thermal Exposure on Dimensional Stability of Honeycomb and Monolithic Materials . . . . .	24
22	Effect of Thermal Cycling on Dimensional Stability of GE-7808 . . . . .	24
23	Effect of Thermal Cycling on Dimensional Stability of GE-3202 . . . . .	24
24	Orientation of Mechanical Test Specimens Cut From a Cylindrical Honeycomb Structure . . . . .	24
25	Macro and Micro Structure of GE-3202 . . . . .	28
26	Macro and Micro Structure of GE-7808 . . . . .	28
27	Macro and Micro Structure of Corning 9460 . . . . .	29
28	Macro and Micro Structure of GE-3200 . . . . .	29
29	Thermal Expansion Behavior of Celsius . . . . .	31

# LIST OF TABLES

Table		Page
1	Oxide Compositions in Weight Percent of the Materials Developed and of Ferro 266M Frit . . . . .	4
2	Mechanical Properties of GE-3200, GE-3202, GE-7808 and Corning Reference Materials . . . . .	6
3	Effect of Thermal Cycling on the Expansion Coefficient of GE-3202, GE-7808 and Corning 9460 . . . . .	17
4	Composition of Sea Salt Used to Evaluate Monolithic Specimens for Sodium Resistance . . . . .	21

## 1. FOREWORD

This final technical report is submitted under NASA Contract NAS 3-19698. It describes work performed primarily in the General Electric Company, Space Sciences Laboratory and Advanced Energy Programs Department by the authors and the following personnel whose contributions are appreciated:

Arno Gatti  
Robert Grosso

William Laskow  
Dr. Michael Noone

In addition, the cooperation of several Coors Porcelain Company personnel (located in Golden, Colorado) for fabricating and firing the several honeycomb test cores is appreciated.

The long term testing conducted by Dr. C. A. Fucinari at the Dearborn, Michigan laboratories of the Ford Motor Company is also acknowledged.

Finally, sincere gratitude is expressed to NASA Program Manager, Dr. Thomas P. Herbell for his technical support and direction, and encouragement over these several years.



## 2. SUMMARY

The objective of this program was the development of ceramic materials suitable for application as rotary regenerative heat exchangers in automotive gas turbine engines. The essential properties required of such materials are: (1) a combination of strength, elastic modulus, and thermal expansion to withstand the several million thermal cycles normally encountered during the lifetime of this critical engine component, and (2) a high degree of dimensional stability under potentially corrosive and mechanically disruptive operating conditions. Laboratory tests conducted on specimens taken from several heat exchanger cores fabricated from materials developed in this program demonstrated that the program objective was met successfully.

At the inception of the program in May 1975, emphasis was on a material which could operate continuously at 1000°C (1832°F) with brief excursions to 1100°C (2012°F). This represented an advanced goal as compared to previous work aimed at 800°C (1472°F) operation. In August 1977, emphasis shifted to a continuous operating temperature of 1100°C (2012°F) with brief excursions to 1200°C (2192°F) which necessitated a basic revision in materials combinations being investigated. To meet the 1000°C (1832°F) goal, a multi-phase, material consisting of lithium aluminosilicate (LAS) and magnesium aluminosilicate (MAS) in a 3:2 LAS/MAS weight ratio was developed. It was designated GE-3200 and was described in NASA CR-135292 issued in November 1977. The more demanding, higher operating temperature was met by developing a multi-phase, zirconia modified magnesium aluminosilicate (ZrMAS) material designated GE-7808 for which a patent application has been filed. The original version of this material was based on a cordierite (MAS) frit, but late in the program it was demonstrated that the MAS phase could probably be satisfactorily furnished through the use of a clay/talc mixture, which when optimized could represent a significant cost reduction. The development of GE-7808 (ZrMAS) material and of a modified LAS/MAS material designated GE-3202 are the subject of this report. The GE-3202 development represents an attempt to improve the corrosion resistance of the original GE-3200 material.

In the development of GE-3200, GE-3202, and GE-7808 about 90 different compositions were investigated. Many were rejected because of high thermal expansion or poor corrosion resistance; others were dimensionally unstable. These parameters were evaluated first because they are critical in selecting a material for use in an application such as a rotary regenerative heat exchanger whose close dimensional tolerances must be maintained to minimize seal leakage during the several million thermal cycles which occur in the expected life of a rotary heat exchanger. They were also evaluated first to help identify the thermal shock resistance of the candidate materials since temperature differences as large as 538°C (1000°F) can exist within a regenerator core during the most severe operating conditions. The specific compositions of GE-7808 (frit and mineral version) GE-3202, GE-3200, and of the MAS frit selected and used to fabricate the regenerator cores for testing are shown in Table 1.

Test specimens of candidate materials in the form of monolithic bars about 6 mm x 6 mm x 51 mm (0.25" x 0.25" x 2") were fabricated usually by cold pressing and sintering although some were cut from large isostatically pressed and sintered bars. Thermal expansion and resistance to molten sea salt and to hot, concentrated sulfuric acid were the first properties to be evaluated. If candidate materials survived these short time tests, phase and dimensional stability were evaluated over long time periods, and mechanical properties were measured. Usually a minimum of three monolithic bars of each composition were used to evaluate each property but as many as six bars were often examined for dimensional stability, whereas strength measurements were always on a minimum of six different specimens. From the several compositions which survived the screening tests, two LAS/MAS and one ZrMAS composition were fabricated into a total of six large, honeycomb, regenerative, heat exchanger cores about 10 cm thick and 51 cm diameter (4' x 20"). The calendering process employed by the fabricator, Coors Porcelain Company, produced a honeycomb structure having 70 cells/cm<sup>2</sup> (450 cells/in<sup>2</sup>) of rectangular geometry. Cell dimensions were approximately 0.5 mm x 2.5 mm (0.02" x 0.1") with a wall thickness in the fired material about 0.2 mm (0.008").

A major benefit of the multi-phase compositions developed in this program was demonstrated during the fabrication and firing operations of the honeycomb structures. Their refractory nature and rheological behavior enabled them to retain their shape and the orientation of gas passages parallel to the axis apparently much better than some single phase (glass ceramic) materials as seen in Figure 1.

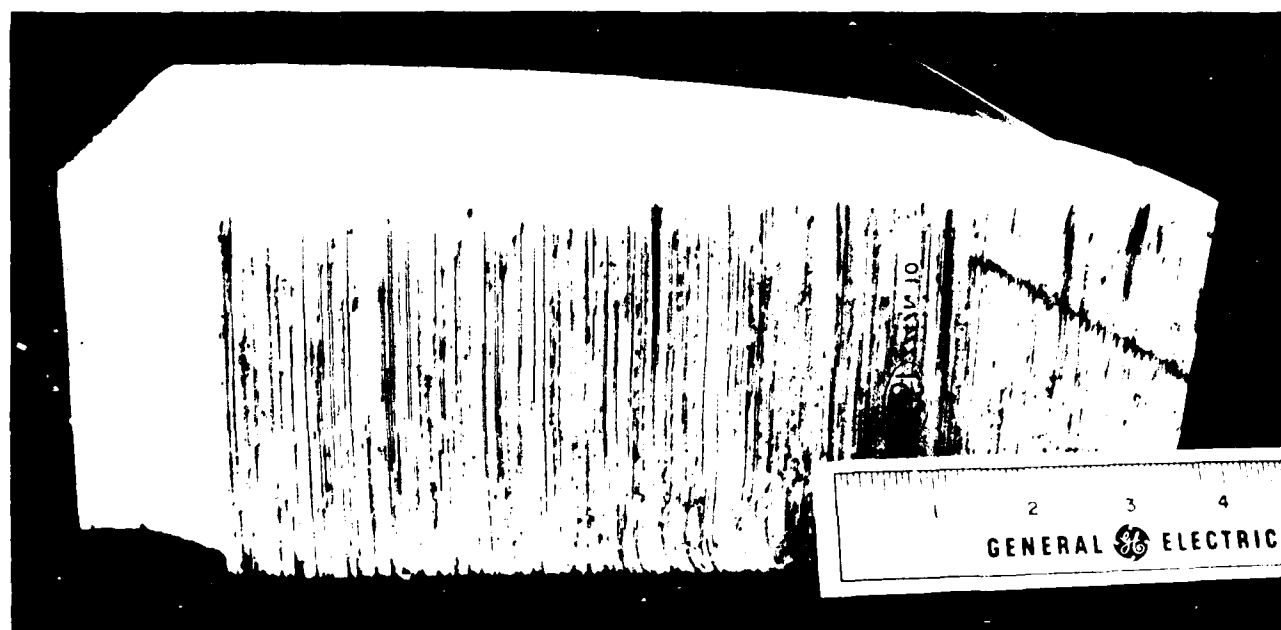


Figure 1. Cross Section of GE-7808 Regenerator core. Cross section is on a radius of a quadrant of a GE-7808 frit based regenerator core as fabricated and fired showing the generally excellent geometry of the gas passages as being parallel to the axis. Some deformation is noticeable along the lower right hand side of the core which would be mostly if not all trimmed off during final machinery.

Table 1. Oxide Compositions in Weight Percent of the Materials Developed and of Ferro 266M Frit

Ferro 266M	GE-7808 (Frit)				GE-7808 (Mineral)		GE-3202		GE-3200	
Coors Data	Raw Batch (2)	Raw Batch (2)	Core #1 (1)	Core #2 (1)	Core #3 (1)	Raw Batch (2)	Core #1 (1)	Raw Batch (2)	Core #1 (1)	Raw Batch (2)
$\text{SiO}_2$	52.7	49.0	46.7	46.0	47.0	42.1	40.3	59.3	64.2	67.3
$\text{Al}_2\text{O}_3$	32.0	34.0	35.9	37.4	37.4	37.4	39.1	29.8	30.3	22.7
$\text{Fe}_2\text{O}_3$	-	-	0.2	0.4	0.2	1.8	1.6	0.06	0.06	-
$\text{TiO}_2$	-	-	0.4	0.2	0.6	1.2	1.04	-	-	-
$\text{ZrO}_2$	-	-	3.4	3.96	2.43	3.6	3.94	-	-	-
$\text{BaO}$	2.0	2.1	1.6	0.99	1.55	-	-	0.84	0.8	0.8
$\text{MgO}$	13.0	13.4	10.3	10.7	10.5	13.7	14.1	5.4	2.0	5.3
$\text{Na}_2\text{O}$	-	0.35	-	0.3	0.3	-	0.04	0.4	0.2	0.2
$\text{K}_2\text{O}$	-	0.05	-	-	-	-	0.01	-	0.3	0.2
$\text{Li}_2\text{O}$	-	-	-	-	-	-	-	4.0	1.96	2.6
$\text{L.O.I.}^{(3)}$	-	1.00	-	-	-	-	-	-	-	-

- (1) From wet chemical analysis  
(2) Calculated from vendor supplied "Typical" analyses  
(3) L.O.I. = Loss on ignition

Firing Conditions for Cores Listed Above:

GE-7808 (Frit Base):	Core 1 - 1400°C/2.9 hours
GE-7808 (Frit Base):	Core 2 - 1375°C/4.0 hours
GE-7808 (Frit Base):	Core 3 - 1375°C/4.0 hours
GE-7808 (Mineral Base):	Core 1 - 1350°C/4.0 hours
GE-7808	Core 2 - 1380°C/6.0 hours
GE-3202	Core 1 - 1260°C/9.3 hours
GE-3200	Core 1 - 1260°C/3.0 hours

(not analyzed)

(not analyzed)

During the entire program, one core each of GE-3200 and GE-3202, three cores of GE-7808 (frit-base), and two cores of GE-7808 (mineral-base), were fabricated and evaluated. The additional cores of GE-7808 (frit-base) were fabricated because the first two cores of this material were insufficiently wide from the hub to the outer core dimension to obtain the required 7.6 cm (3.0") diameter specimens for simulated gas turbine engine tests. The first core of GE-7808 (mineral-base) material contained numerous radial shrinkage cracks and delaminations which also precluded obtaining specimens for simulated engine evaluation, thus the second core was made.

The honeycomb material was evaluated by cutting small specimens of various geometries from each core and determining the following properties: thermal expansion, corrosion resistance, phase stability, modulus of elasticity, modulus of rupture, and density. In addition, the effect of thermal cycling and exposure to corrosive environments on thermal expansion was determined. Performance of the materials in simulated gas turbine screening tests was also evaluated at Ford Motor Company. All specimens of GE-3202 and GE-7808 evaluated in-house were compared to similarly tested specimens of Corning 9460, an alumina-silicate (AS) material which was selected by NASA as the reference material. Early in the program, the reference materials were Corning 9454 and Corning 9455. The former is monolithic LAS; the latter is honeycomb LAS. Corning 9460 is produced by acid-leaching the 9455 honeycomb material. A summary of the mechanical properties measured on both monolithic and honeycomb specimens of GE-3200, GE-3202, GE-7808, and the Corning reference materials (9455 and 9460) is shown in Table 2.

The results of the thermal and corrosion testing aspects of this program agree with the data obtained from extensive simulated engine testing at the Ford Motor Company which indicate that LAS-containing materials, while showing improved corrosion resistance as compared to earlier materials, are not as corrosion resistant as some other newer compositions. However, the ZrMAS materials developed in this program appear to be worthwhile candidates for such applications. Test results comparing the performance of frit based GE-7808 with Corning 9460 show that the ZrMAS materials are equally resistant to sulfur attack, significantly more resistant to sodium attack, and have slightly better dimensional stability during dynamic thermal cycling. Additional stability tests were performed at the Ford Motor Company on GE-7808 mineral base ZrMAS. Specimens were exposed for 840 hours to 1000°C (1832°F) and 1100°C (2012°F) with and without sodium present and performance was evaluated on dimensional changes. In addition, the thermal expansion of these specimens, before and after these tests, was measured over the temperature range, 25-1100°C (77-2012°F). The Ford data appear in Figures 2, 3, and 4 and indicate excellent dimensional stability which confirms the General Electric Company early results. Although the processing of GE-7808 mineral base ZrMAS has not been completely optimized, the data obtained so far suggest that this material has the potential for excellent dimensional stability to at least 1100°C (2012°F).

Table 2. Mechanical Properties of GE-3200, GE-3202, GE-7808 and Corning Reference Materials

Monolithic	Modulus of Rupture MPa (psi)		Elastic Modulus MPa (psi)	Strain Tolerance (ppm)	
	Tangential	Radial		Tangential	Radial
GE-3200	77.9	(11.3 x 10 <sup>3</sup> )	72400	(10.5 x 10 <sup>6</sup> )	1076
GE-3202	107.5	(15.6 x 10 <sup>3</sup> )			
GE-7808 <sup>(1)</sup>					
GE-7808 <sup>(2)</sup>					
Corning 9454	84.1	(12.2 x 10 <sup>3</sup> )	71700	(10.4 x 10 <sup>6</sup> )	1183
Honeycomb	Modulus of Rupture MPa (psi)		Elastic Modulus MPa (psi)	Strain Tolerance (ppm)	
	Tangential	Radial		Tangential	Radial
GE-3200	8.2 (1189)	0.65 (94)	7385 (1.1 x 10 <sup>6</sup> )	1080	904
GE-3202	4.1 (601)	0.63 (91)	3105 (4.5 x 10 <sup>5</sup> )	1335	5688
GE-7808 <sup>(1)</sup>	5.5 (803)	0.76 (110)	4002 (5.8 x 10 <sup>5</sup> )	1384	3056
GE-7808 <sup>(2)</sup>	3.7 (535)	0.39 (57)	4347 (6.3 x 10 <sup>5</sup> )	849	3167
Corning 9455	6.1 (881)	1.3 (191)	2758 (4.0 x 10 <sup>5</sup> )	2203	1194
Corning 9455 <sup>(3)</sup>	8.1 (1178)	1.7 (246)	14490 (2.1 x 10 <sup>6</sup> )	569	2025
Corning 9460	3.1 (445)	0.74 (107)	2277 (3.3 x 10 <sup>5</sup> )	1345	4280
Corning 9460 <sup>(3)</sup>	7.7 (1112)	0.81 (118)	5244 (7.6 x 10 <sup>5</sup> )	1463	4069

Note: A load application rate of 1380 kPa (200 psi)/minute was used in all of the testing except for the Corning supplied tangential data, which was generated with a loading rate of 6900 kPa (1000 psi)/minute.

(1) Frit Base

(2) Mineral Base

(3) Corning Data

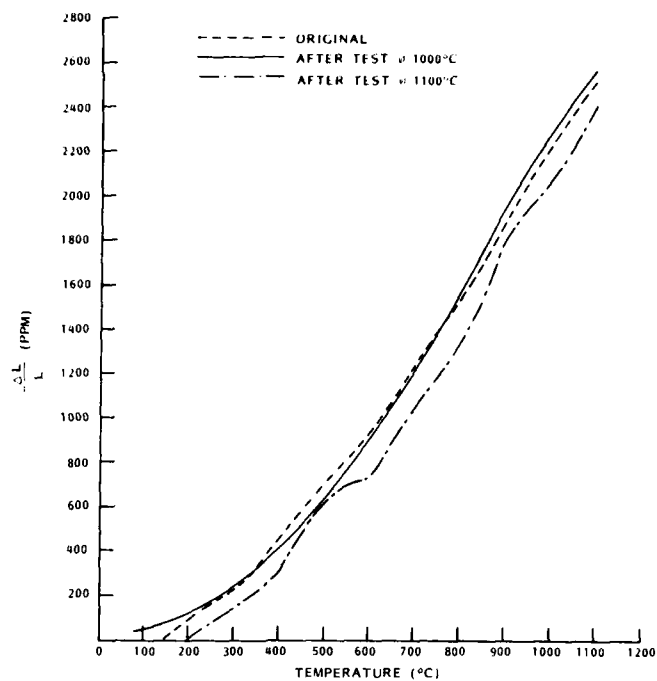


Figure 2. Thermal Expansion of GE-7808 Before and After 1000°C and 1100°C Exposure with Sodium Present (Ford Motor Company Data)

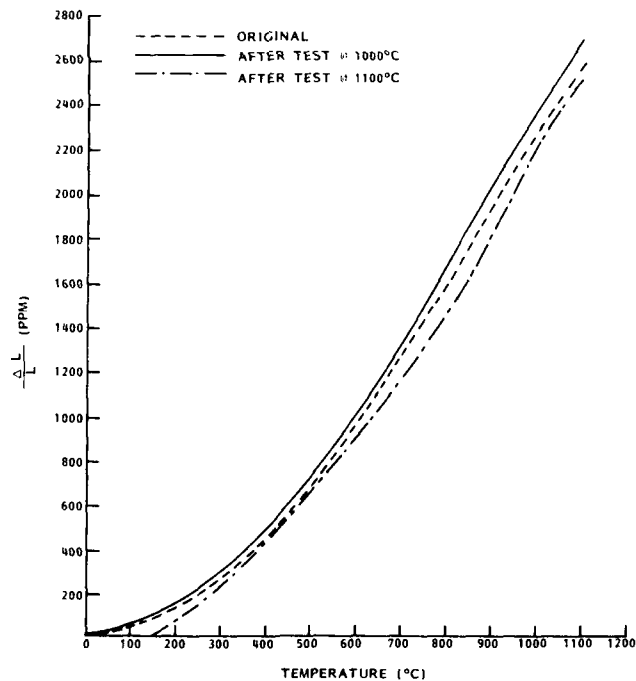


Figure 3. Thermal Expansion of GE-7808 Before and After 1000°C and 1100°C Exposure (Ford Motor Company Data)

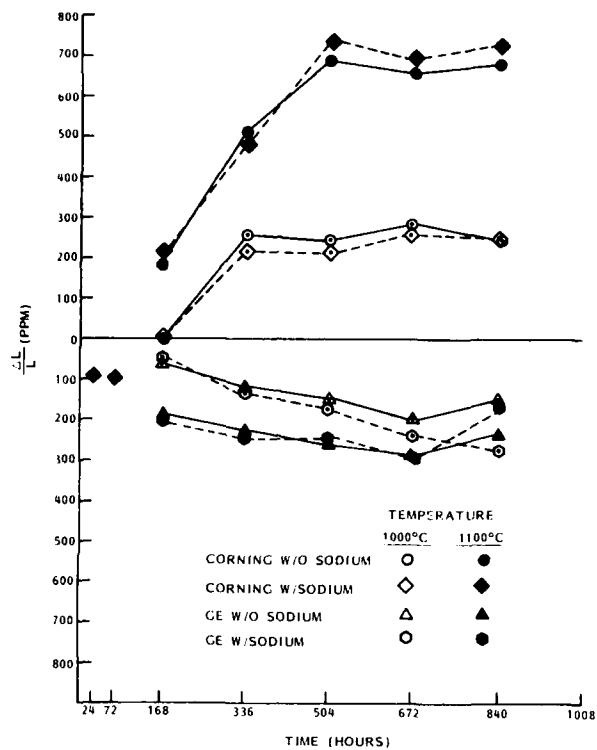


Figure 4. Dimensional Stability of GE-7808 and Corning-9460 After Exposure at 1000°C and 1100°C with and without Sodium (Ford Motor Company Data)

### 3. INTRODUCTION

The recovery and utilization of waste heat through rotary regenerative heat exchangers is mandatory if automotive gas turbine engines are to compete successfully with other types of automotive engines. Metallic heat exchangers are limited to relatively low temperatures but, more important, would exhaust the current supply of critical alloying elements. Consequently, automotive designers and engineers began to explore the feasibility of utilizing ceramic components as early as the mid-1950s. In the early 1960s, their interest was further stimulated by the advent of very low expansion glass-ceramics. Since the mid-1960s an intensive effort has been underway to utilize these materials as rotary heat exchanger components. Early corrosion failures resulted in programs, such as this one, to develop other ceramics which offer both improved corrosion resistance and higher operating temperatures. Today, several ceramic suppliers and automobile manufacturers are engaged in developing materials and processes for fabricating these materials into ceramic honeycomb structures and applying them very successfully as rotary heat exchangers.

The materials of current interest are an aluminosilicate (AS), several magnesium aluminosilicates (MAS), and a zirconia-modified magnesium aluminosilicate (ZrMAS). Some of these materials are produced from powdered glass which can be thermally converted to a glass-ceramic, some are produced by heat-treating intimately mixed mineral combinations; and, some utilize portions of each technology. However, it appears that the thermally reacted mineral combinations offer the most likely approach which will successfully meet the economic requirements of large scale production of rotary ceramic honeycomb heat exchanger cores.

Aluminosilicate (AS) material is produced by acid leaching and heat treating lithium aluminosilicate (LAS) honeycomb. This results in a very corrosion resistant, low thermal expansion structure useful to temperatures approaching  $1000^{\circ}\text{C}$  ( $1832^{\circ}\text{F}$ ). Exposure to higher temperatures can result in dimensional instability unless the heat treatment after acid leaching is carefully adjusted to produce sufficient mullite crystals at the grain boundaries, thereby inhibiting grain growth<sup>(1)</sup>. Magnesium aluminosilicate (MAS) materials can be made from finely powdered recrystallizable glass, mineral mixtures such as clay and talc, or from combinations of these materials. The ZrMAS material described in this report is essentially an MAS to which zircon has been added. The MAS and ZrMAS materials can withstand exposures over  $1100^{\circ}\text{C}$  ( $2012^{\circ}\text{F}$ ), and possess excellent corrosion resistance. Although they exhibit considerably higher expansion coefficients than the AS material, they have very good dimensional stability and appear to offer a suitable combination of properties (modulus, strength, and expansion) essential in rotary regenerative heat exchanger materials.

The three primary fabricating processes for making honeycomb structures are corrugating, calendering (extrusion-embossing), and extrusion. An excellent review of these processes appears in Reference 2. Briefly, the first method uses paper which has been impregnated with ceramic powder to form a structure similar to corrugated cardboard. The second method, embossing, consists of drawing a thin ceramic film onto a plastic substrate or extruding a thin ceramic tape into which a subsequent treatment impresses spaced ridges which act as separators between concentric tape layers, thus forming the cellular structure common to honeycomb materials. When the ceramic film is extruded by itself and later embossed, the process is also



known as calendering. The third method, extrusion, is one in which a plastic binder and ceramic powder mixture is forced through a die to immediately form a honeycomb structure. The first two methods can produce circular shapes typically in diameters of 71.1 cm (28 in.) and 10.2 cm (4 in.) thick, while extrusion is limited presently to smaller segments which can be bonded together to form larger shapes. Schematic illustrations of these techniques appear in Figures 5, 6 and 7. The calendering (embossing) process was chosen and heat exchanger cores were fabricated by the Coors Porcelain Company from materials developed under this program.

The majority of the work described in this report had as its objective the development of a material which would be resistant to combined thermal/corrosive (salt and acid) environments, would remain dimensionally stable during long-term and rapid thermal cycling to 1100°C (2012°F) and survive brief exposures at higher temperatures. The material also had to have a moderately low thermal expansion to 1200°C (2192°F).

This report also includes a description of some work to improve a lithium aluminosilicate/magnesium aluminosilicate (LAS/MAS) material which was developed several years ago in the program, designated as GE-3200 and was described in Reference 3.

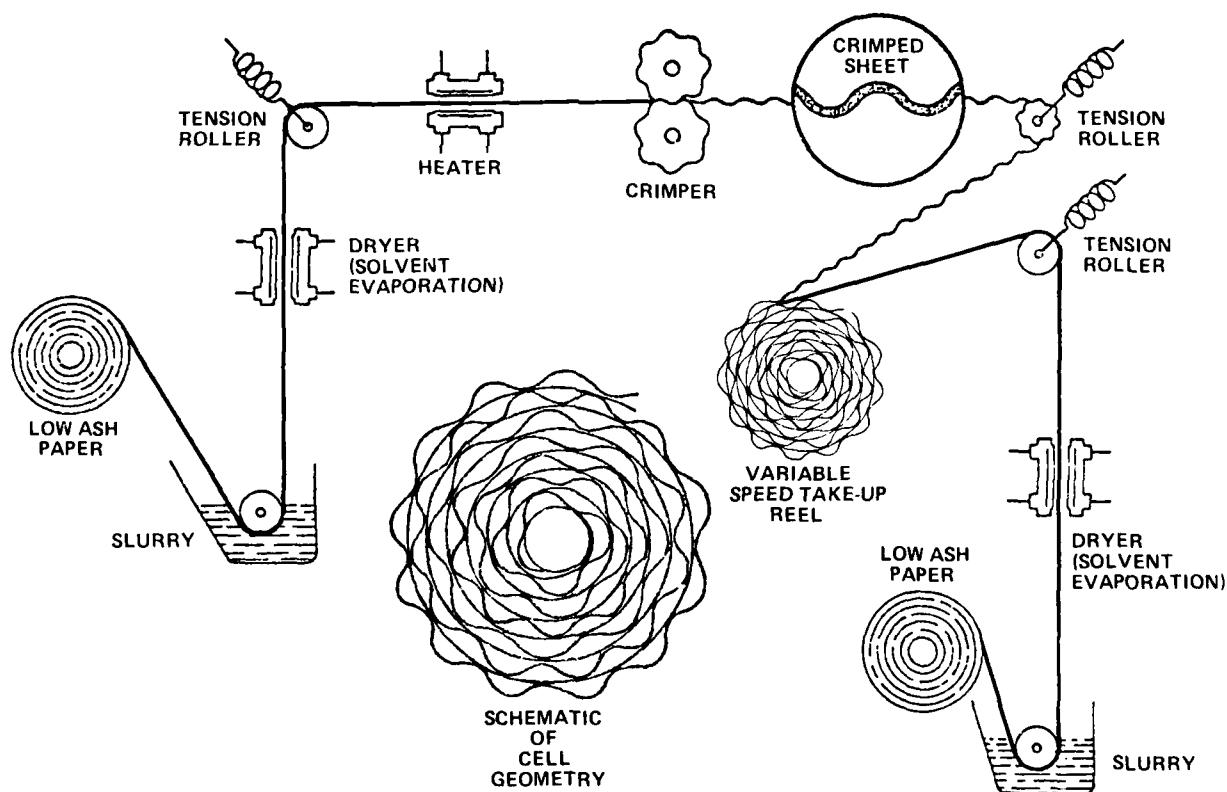


Figure 5. Typical Coated Paper Wrapping Operation

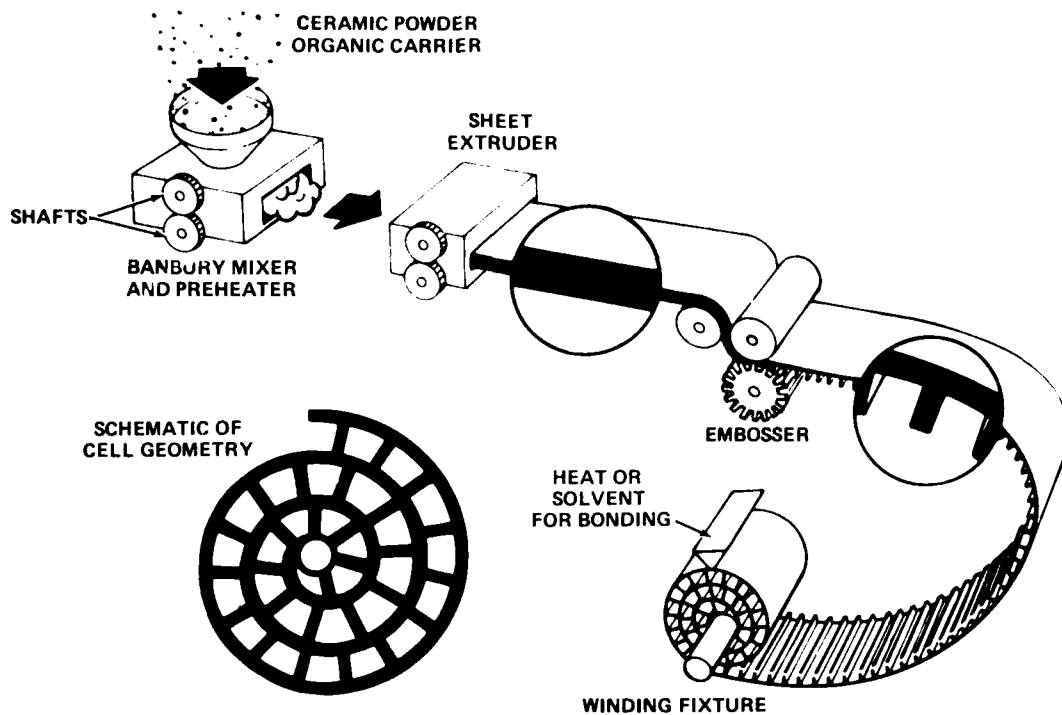


Figure 6. Typical Embossing Operation

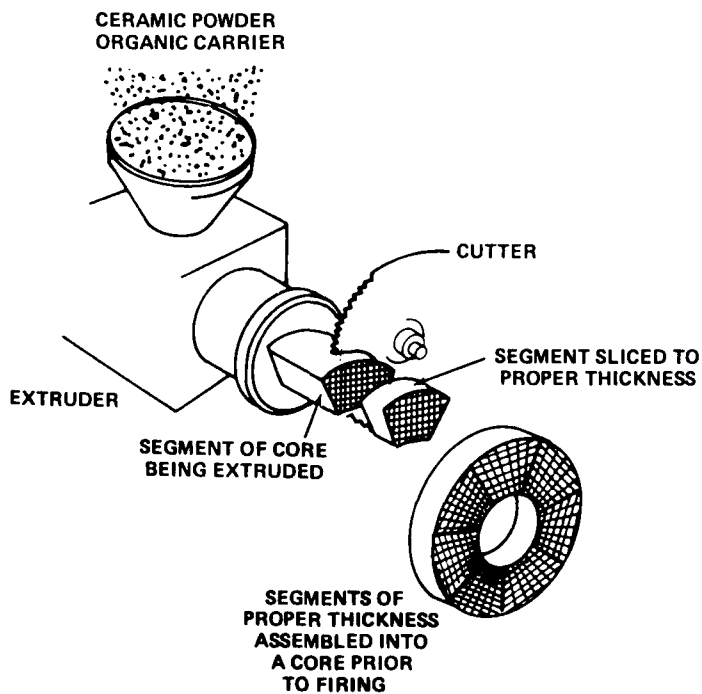


Figure 7. Typical Extrusion Operation

## 1. MATERIALS DEVELOPMENT

From the beginning of the program, emphasis has been on materials which possess a combination of low thermal expansion, good corrosion resistance, moderate strength, and good dimensional stability. These parameters were influential in an early decision to evaluate such candidates as lithium alumino-silicate (LAS), magnesium aluminosilicate (MAS), aluminum titanate (AT), and various AT modifications. Later in the program a requirement for better corrosion resistance and greater refractoriness prompted the investigation of such ternary materials as boron, zinc, and zirconia aluminosilicates (BAS, ZnAS, and ZrAS) and ultimately a zirconia modified MAS (ZrMAS). The composition and particle size distribution of these starting materials was always given primary consideration.

At the outset of the LAS/MAS materials development, petalite ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8 \text{SiO}_2$ ) was selected as the LAS phase and GE-3200 which resulted from our work with these compositions consisted of petalite and a cordierite frit in a 3:2 ratio. However, subsequent chemical analysis of the petalite showed that it contained, in addition to the expected 3.2 w/o lithium oxide, an equal amount of sodium and potassium oxides<sup>(3)</sup>. Although GE-3200 exhibited better corrosion resistance than the LAS reference material (Corning 9455), we believed that reduction of the total alkali content would result in an improved LAS/MAS material. Consequently GE-3202 (LAS/MAS) was formulated using low iron, beta-spodumene and excess silica to provide the LAS phase and a recrystallizable, cordierite ( $2 \text{MgO} \cdot 2 \text{Al}_2\text{O}_3 \cdot 5 \text{SiO}_2$ ) glass powder (Ferro 266M) to supply the MAS phase. Extensive testing of both monolithic and honeycomb specimens showed that the thermal expansion was about the same as GE-3200, but it was about 25°C (77°F) more refractory and had improved dimensional stability. However, there was no significant difference in the corrosion resistance of the two LAS/MAS materials. These results suggested eliminating the LAS phase completely and concentrating on the development of more corrosion resistant and more refractory materials.

Work then directed at higher temperature capability materials included evaluation of various compositions in the ternary systems,  $\text{B}_2\text{O}_3$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (BAS),  $\text{ZnO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (ZnAS) and  $\text{ZrO}_2$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (ZrAS). In the compositions screened,  $\text{B}_2\text{O}_3$  contents varied from about 5 to 12 w/o, ZnO from 18 to 37 w/o and  $\text{ZrO}_2$  up to 36 w/o. Preliminary evaluation of specimens from each system fired at 1300°C (2372°F) indicated considerable glass formation (self-glazing) in the BAS materials, low strength in the ZnAS materials, poor corrosion resistance in both the BAS and ZnAS materials, and considerable porosity but excellent corrosion resistance in the ZrAS materials. The known ability of cordierite frit to produce low porosity bodies suggested the use of this material to increase the density of the ZrAS compositions and prompted an investigation of materials in the quaternary system,  $\text{ZrO}_2$ - $\text{MgO}$ - $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  (ZrMAS). Early indications of relatively low thermal expansion, good dimensional stability, and excellent corrosion resistance from specimens in this system led to concentration of the development of an optimum composition. In the latter stages of the program, a successful but limited effort was devoted to supplying a cordierite (MAS) phase from a lightly calcined clay/talc mixture, for economic reasons which are discussed later.

Developmental quantities of each composition were prepared in 900-gram batches by ball milling various combinations of the raw materials. Since the starting materials were already screened to pass a 200 mesh sieve, a milling time of only two hours was used. Small amounts of stearic acid ( $\leq 1\%$  of the batch) were included with the starting materials to minimize contamination from the mill and grinding media and Carbowax 6000 were employed as a pressing aid.

Numerous material combinations were investigated and several were identified as potential heat exchanger materials candidates. Specific selections, GE-3200, GE-3202, and GE-7808 chosen for regenerator core fabrication are shown in Table 1. The compositions were derived from calculations based on vendor supplied "typical" analyses and from the results of wet chemical analysis.

Throughout the program all honeycomb fabrication was performed by Coors Porcelain Company using a calendering process<sup>(4)</sup>. Circular structures ranging from 45 to 55 cm O.D. and of varying I.D. and 10.2 cm thick (18" to 22" diameter and 4" thick) were made by this process from the LAS/MAS and ZrMAS materials developed in this program. These circular honeycomb cores contained about 70 cells/cm<sup>2</sup> (450 cells/in.<sup>2</sup>) which were rectangular with dimensions of approximately 0.5 mm by 2.5 mm (0.02" x 0.1"). Cell wall thickness averaged about 0.20 mm (0.008"). Firing temperatures varied with material composition, ranging from 1260°C (2300°F) for GE-3202, to 1400°C (2552°F) for GE-7808 material.

## 5. MATERIALS EVALUATION AND RESULTS

The dimensional stability of ceramic heat exchanger materials is vital in maintaining low seal leakage which is a requirement in the efficient recovery of exhaust heat. In addition, this property is essential to the overall integrity of the heat exchanger core during the more than six million thermal cycles (average 30 rpm for 3500 hours) and exposure to ingested road salt and sulfuric acid from exhaust gasses. Serious structural damage (e.g., ion exchange) can result from the severe operating conditions with accompanying catastrophic failure in the core material. Thus, primary emphasis was placed on evaluating the effect of various environments on the dimensional stability of the materials developed in assessing their value as heat exchanger core materials. The testing environments included static and cyclic thermal exposures and combined thermal/corrosion exposures in the laboratory and actual engine tests in which test specimens may be small cylindrical inserts mounted in a host heat exchanger core or a full size core. Several ancillary evaluations such as weight changes due to corrosion testing, X-ray and microscopic examination for indications of phase changes were also employed. These techniques, however, were supplemental to the primary goal of determining dimensional stability by carefully performed measurements.

Monolithic bars of each candidate material were evaluated for thermal expansion and corrosion resistance to determine if further testing was warranted. LAS/MAS candidates which showed expansions of 2000 ppm or less at 1000°C (1832°F) and ZrAs and ZrMAS candidates which expanded 3000 ppm or less at 1200°C and any candidates which exhibited less than 5% weight change during corrosion testing were subsequently evaluated for phase and dimensional stability and modulus of rupture.

The screening tests were performed on bar-shaped specimens about 6 mm x 6 mm x 51 mm (0.25" x 0.25" x 2") which usually were fabricated by cold pressing followed by sintering. However, some of the specimens were cut from lightly sintered, isostatically pressed bars about 1.3 cm x 4.5 cm x 20 cm (0.5" x 1.8" x 8"). Fabrication parameters such as particle size, forming pressures, and sintering temperatures were selected so that the porosity of fired specimens, regardless of composition, would be similar.

The evaluation of various compositions in monolithic form indicated that two candidates merited fabrication into honeycomb for additional testing. These compositions, GE-3202 (LAS/MAS) and GE-7808 (Zr/AS), were fabricated into full-size heat exchanger cores which were cut into smaller test specimens to be tested with and compared to Corning 9460, an aluminosilicate (AS) material. The results of these tests are presented in the following sections.

### 5.1 Thermal Phase Stability

X-ray diffraction analyses were conducted with a GE XRD-5 diffractometer to determine whether thermal exposure produced any mineralogical changes in the candidate materials. The LAS/MAS (GE-3202) materials and the Corning 9460 reference material were exposed to 1000°C (1832°F) while the ZrAS and ZrMAS (GE-7808) materials were exposed to 1200°C (2192°F). All specimens were subjected to exposure times of 1, 5, 10, and 20 hours and XRD examination was made after each exposure interval. Neither the monolithic nor the

honeycomb specimens showed any change in amounts or kinds of phases present as a result of this treatment.

In some supplemental work performed by Professor R. A. McCauley, while under National Science Foundation sponsorship in our laboratory, thin sections of both GE-7808 frit and mineral base honeycomb specimens were also examined by optical microscopy. The frit base contained very small inclusions within the cordierite grains, but a similar phase was not detected in the mineral base material. Since the inclusions were beyond the resolution (1000X) of the optics, an electron probe X-ray microanalyzer was used to determine that the inclusions consisted of Ba, Al and Si which later helped to identify the phase as celsian,  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2 \text{SiO}_2$ . Further work on this finding is described in the "Materials Evaluation and Results" section of this report.

The dimensional stability of the honeycomb materials subjected to the thermal phase stability tests was also evaluated by measuring specimen length before and after each exposure and comparing any changes to the initial length of each specimen. The data obtained are shown in Figure 8.

The device used to measure specimen length is an Inconel block containing a V-groove to which a dial gauge is attached on one end of the V-groove; the dial gauge is calibrated to 0.0025 mm (0.0001"). The specimen is placed in the V-groove against the dial gauge extension, as shown in Figure 9, and a measurement is taken. Values less than the smallest dial dimension can be estimated quite reproducibly and all data are reported as parts per million (ppm).

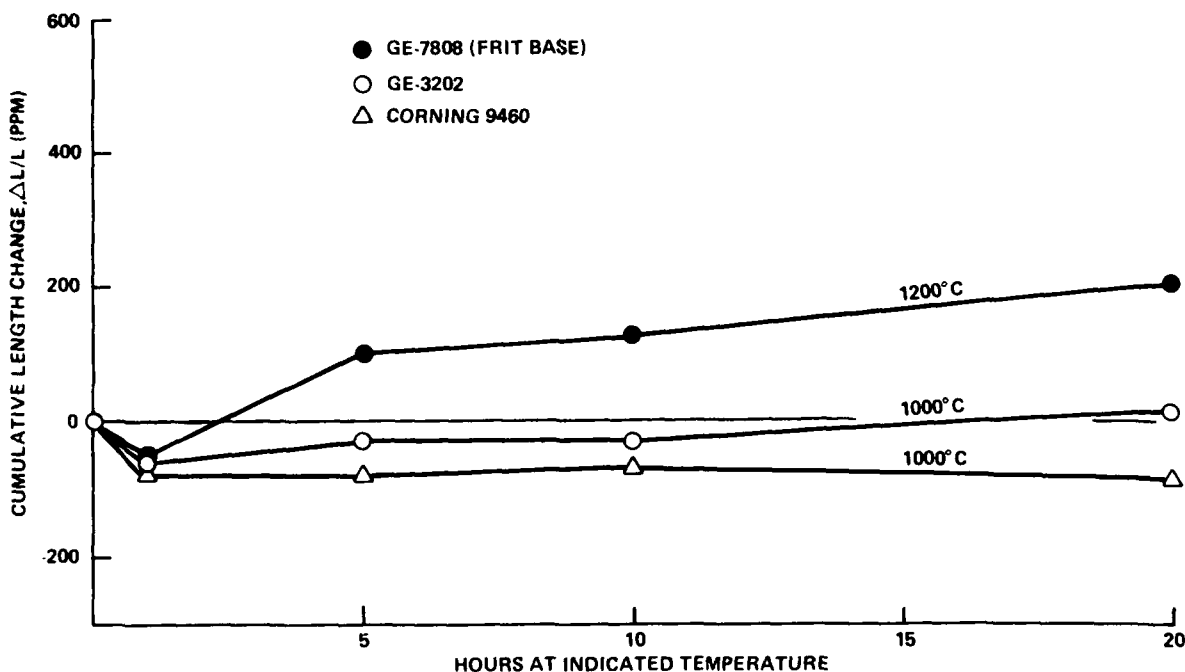


Figure 8. Effect of Thermal Cycling During Phase Stability Study on Dimensional Stability

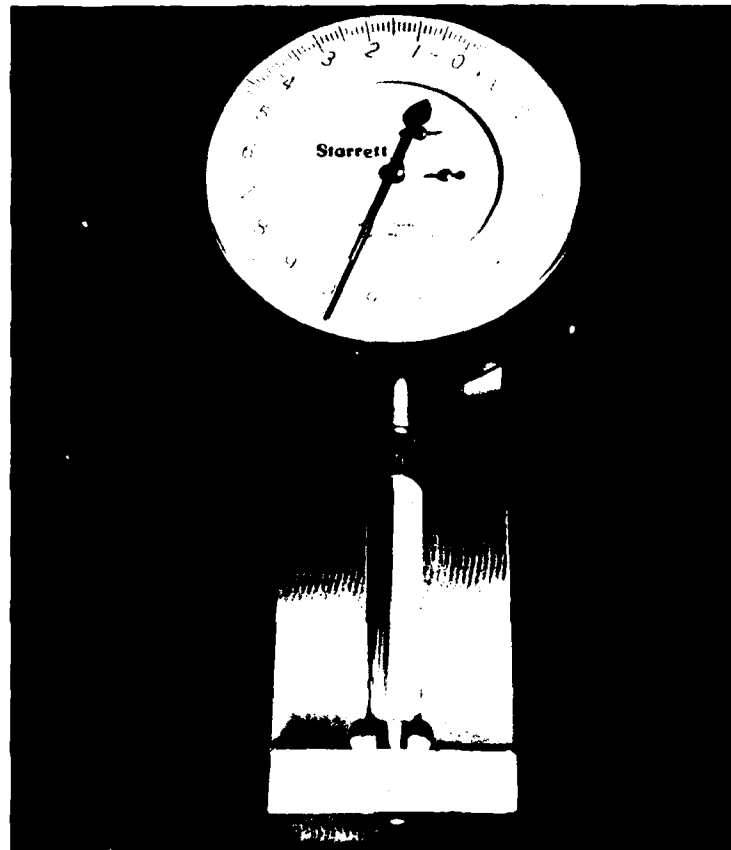


Figure 9. Measuring Device

## 5.2 Thermal Expansion

Throughout the program, at least 300 expansion measurements were made. Early in the program this property was measured with a Theta Dilatronic II dilatometer, but since March 1978 a Harrop Laboratories Model TDA H1-MP6 dilatometer has been used. The expansion of all specimens was measured using heating and cooling rates of  $2^{\circ}\text{C}/\text{minute}$ , but the LAS/MAS materials and the Corning 9460 (AS) reference material were tested to  $1000^{\circ}\text{C}$  ( $1832^{\circ}\text{F}$ ) while the ZrAs and ZrMAS materials were tested to  $1200^{\circ}\text{C}$  ( $2192^{\circ}\text{F}$ ).

The results show that changes in thermal expansion can be produced by variations in original firing temperatures, by dynamic and static thermal cycling, and by exposure to corrosive environments. Examples of the changes that occurred are presented in Figures 10 through 15 and in Table 3. Although these data show that GE-7808 (frit and mineral base) has a higher expansion coefficient than either GE-3202 or Corning 9460, they also indicate that this property is only slightly affected by corrosion testing. The thermal expansion behavior for several of the leading candidate materials for application in advanced heat engines is shown in Figure 16.

Table 3. Effect of Thermal Cycling on the Expansion Coefficient of  
GE-3202, GE-7808 and Corning 9460

Coefficient of Thermal Expansion ( $10^{-6}/^{\circ}\text{C}$ )

Material:	GE-3202	Corning 9460	GE-7808	
Exposure Temperature:	1000 <sup>o</sup> C (1832 <sup>o</sup> F)		1200 <sup>o</sup> C (2162 <sup>o</sup> F)	
Exposure Time (Hours)				
0	1.80	0.5	2.56	2.95*
10	1.76	0.5	2.63	2.95
50	2.15	0.6	2.63	2.87
100	1.86	0.6	2.82	3.19
300	1.86	0.8	2.46	2.89
500	1.86	0.7	2.87	3.10

\* Coefficient measured between 25 - 1200 $^{\circ}\text{C}$  (77-2162 $^{\circ}\text{F}$ ). Other coefficients measured between 25 - 1000 $^{\circ}\text{C}$  (77-1832 $^{\circ}\text{F}$ ).

Note: Typical expansion curves for these materials are shown in Figures 6 through 11.



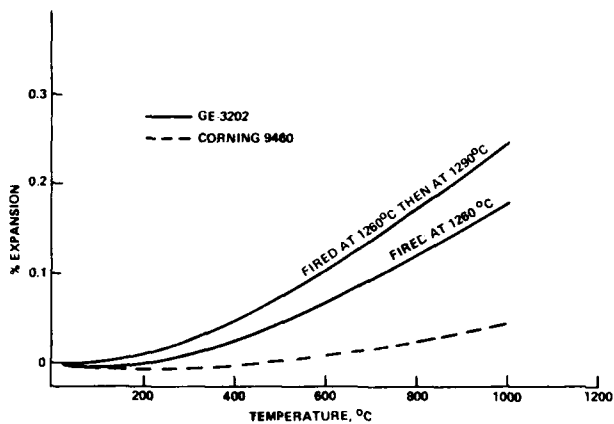


Figure 10. Thermal Expansion of GE-3202 vs. Temperature

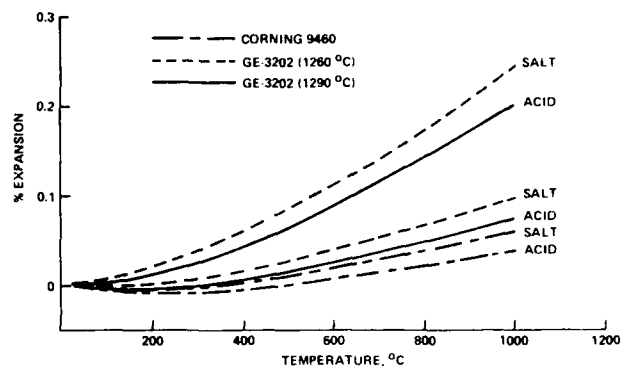


Figure 11. Effect of Firing Temperature on the Corrosion Resistance of GE-3202 as Indicated by Thermal Expansion

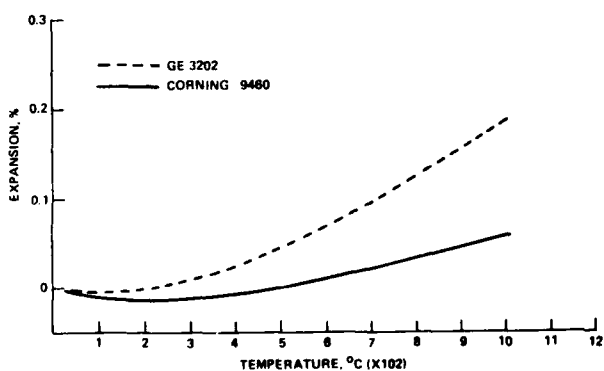


Figure 12. Thermal Expansion of GE-3202 and Corning 9460 After 500-Hour Exposure at 1000°C

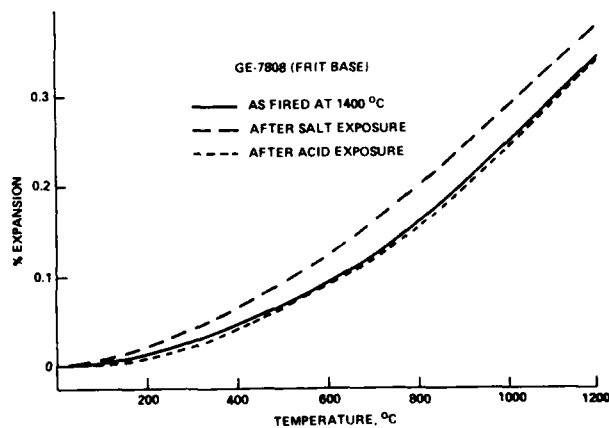


Figure 13. Thermal Exposure of Corrosion Tested GE-7808

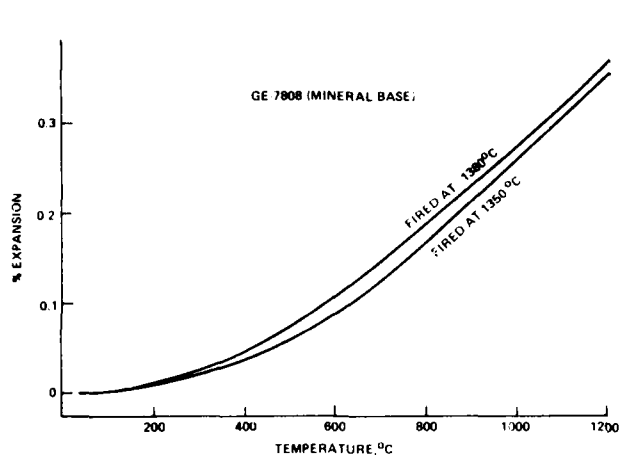


Figure 14. Effect of Firing Temperature on Thermal Expansion of GE-7808

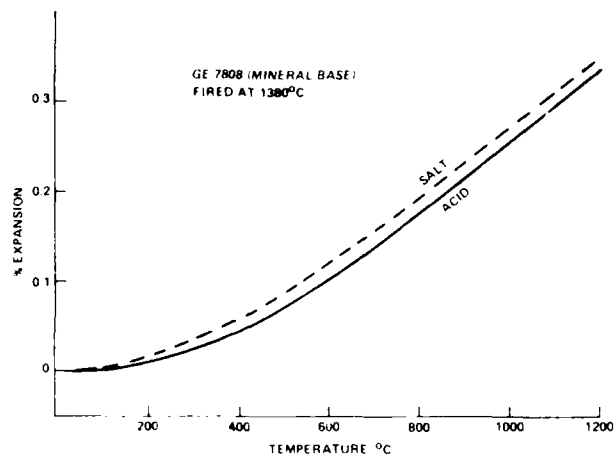


Figure 15. Effect of Corrosion Testing on Thermal Expansion of GE-7808

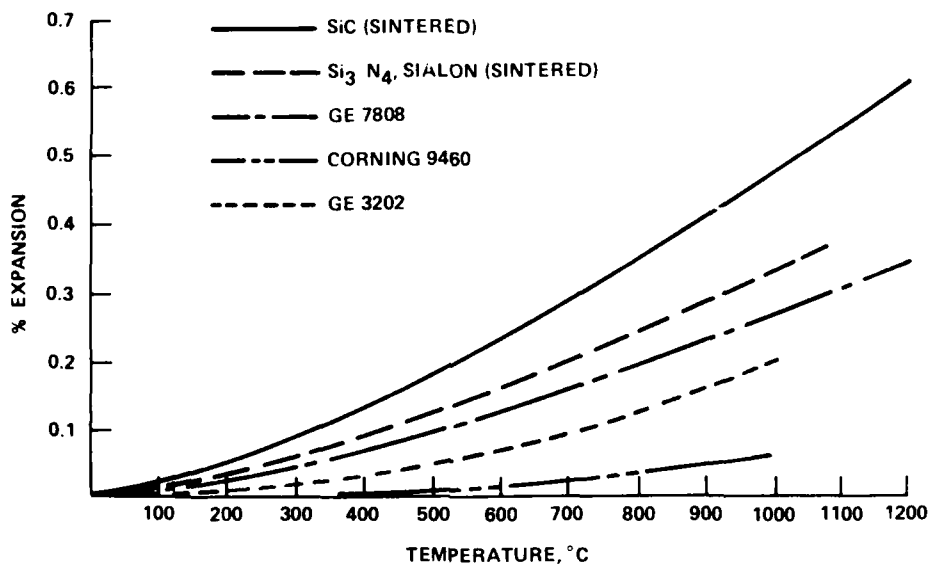


Figure 16. Thermal Expansion of Several Candidate Heat Exchanger Materials

### 5.3 Corrosion Resistance

Monolithic specimens were evaluated for resistance to sodium and sulfuric acid attack primarily by determining whether specimen weight changes occurred. Specimens were also examined for evidence of cracks and etching. The corrosion resistance of honeycomb specimens, however, was evaluated on the basis of changes in specimen length and thermal expansion as well as visual evidence of etching and cracks.

### 5.4 Acid Testing

Monolithic specimens were immersed for two hours in 300°C (572°F) concentrated sulfuric acid, then removed and heated for two hours at 320°C (608°F). The specimens were then re-immersed in the hot acid for an additional two hours, removed and heated for two hours at 650°C (1202°F). A final two hour immersion in the hot acid was followed by heating for two hours at 1000°C (1832°F). Therefore, each specimen received a total immersion time of six hours in the 300°C (572°F) acid.

Honeycomb material was evaluated for acid resistance by immersing specimens in a 1% sulfuric acid solution for two hours at room temperature. Only one specimen was tested in a given solution which was always freshly prepared and the solution was evacuated for two minutes at the beginning of the cycle to remove entrapped air from the honeycomb cells. At the end of the immersion cycle, the specimen was removed, excess solution was gravity drained and the specimen was heated for two hours at 315°C (599°F). Each specimen was subjected to a minimum of three such cycles and  $\Delta L/L$  was recorded after each cycle.

### 5.5 Salt Testing

Evaluation of monolithic specimens to sodium was made by placing a specimen in a 100 cc platinum crucible, covering the specimen with dry, -20 mesh sea salt and placing the crucible in a furnace heated to 750°C (1382°F). As the sea salt melted, additional salt was added to maintain the liquid level above the specimen during the two hour test duration. The composition of the sea salt is shown in Table 4.

The sodium resistance of honeycomb specimens was evaluated as follows:

1. Immerse specimen for five minutes in a boiling 3.5% NaCl solution in a reflux condenser.
2. Blow excess solution out of specimen for five minutes using filtered, oil-free nitrogen or air at 5 psig.
3. Dry specimen at 200°C (392°F).
4. Heat specimen at 800°C (1472°F) for three weeks, measuring  $\Delta L/L$  after 1, 3, 7, 14 and 21 days.

Table 4. Composition of Sea Salt Used to Evaluate  
Monolithic Specimens for Sodium Resistance

	<u>w/o</u>
NaCl	58.5
MgCl <sub>2</sub> · 6 H <sub>2</sub> O	26.5
Na <sub>2</sub> S	9.8
CaCl <sub>2</sub>	2.8
KCl	1.6
NaHCO <sub>3</sub>	0.5
KBr	0.2
H <sub>3</sub> BO <sub>3</sub>	0.1
SrCl <sub>2</sub> · 6 H <sub>2</sub> O	0.1
NaF	0.001

The corrosion resistance of honeycomb materials was determined by measuring specimen lengths initially and after each salt or acid cycle. Changes in length were compared to the original length with the results reported as  $\Delta L/L$  in ppm. Typical data of this nature are shown in Figures 17 through 20.

These data reveal that Corning 9460 is significantly more corrosion resistant than GE-3202, that the acid resistance of GE-7808 and Corning 9460 is about equal, but GE-7808 (frit base) fired at 1375°C (2507°F) and GE-7808 (mineral base) fired at 1380°C (2516°F) are more resistant to salt attack than Corning 9460.

#### 5.6 Dimensional Stability

This parameter was evaluated using specimens about 51 x 6 x 6 mm (2.0 x 0.25 x 0.25 in). Specimen lengths were measured initially and after periodic long term and short term thermal exposures. Length changes were compared to the original length and are reported as  $\Delta L/L$  in ppm as previously described.

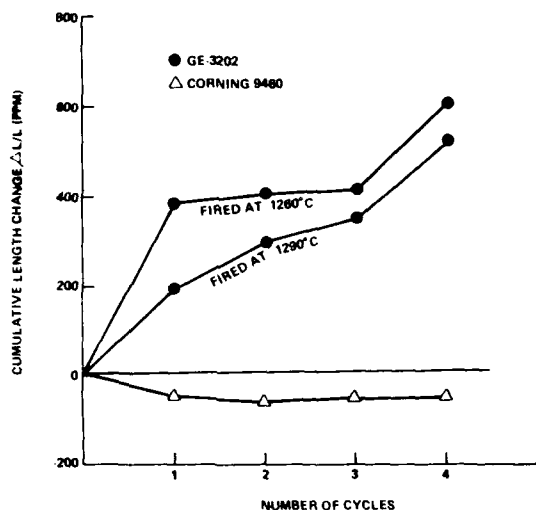


Figure 17. Effect of Acid Treatment on Dimensional Stability of GE-3202

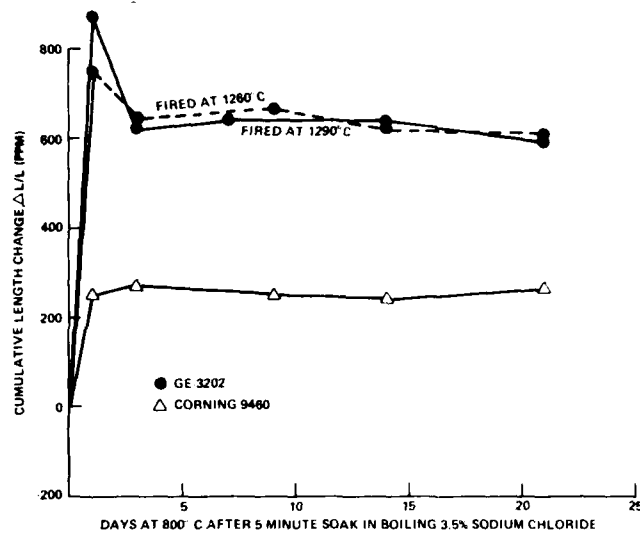


Figure 18. Effect of Salt Treatment on Dimensional Stability of GE-3202

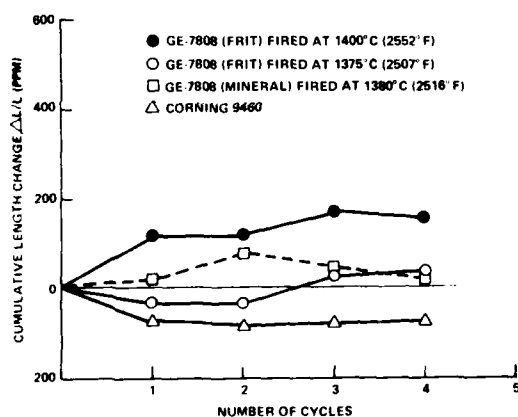


Figure 19. Effect of Acid Treatment on Dimensional Stability of GE-7808

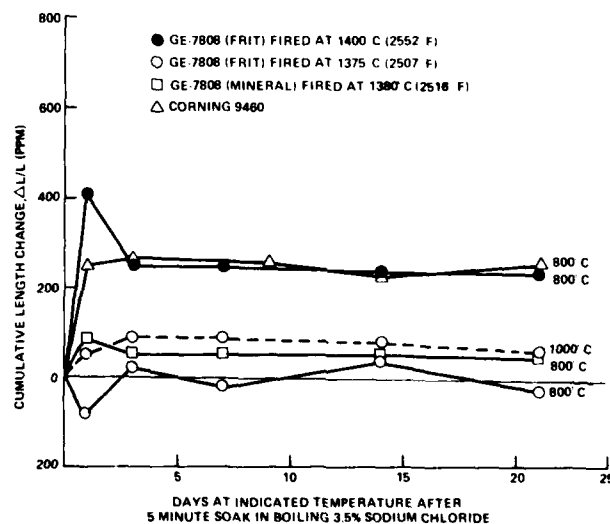


Figure 20. Effect of Salt Treatment on Dimensional Stability of GE-7808

Short term (dynamic) cycling was accomplished by inserting specimens into a hot furnace, holding the specimens in the hot zone for a pre-selected length of time, then retracting the specimens. Each cycle typically consisted of a 1.3 minute travel into the hot zone, a 3.4 minute hold, and a 1.3 minute retraction out of the hot zone to ambient. Hold time outside the furnace was 5 seconds before the cycle repeated. Each specimen was exposed to at least 1500 cycles (85 hours at temperature) and some specimens were subjected to 3500 cycles (198 hours at temperature).

Long term (static) cycling was performed by placing specimens in a heated furnace according to the following schedule:

1. Ten cycles with a 1 hour hold at peak temperature
2. Three cycles with a 6 hour hold at peak temperature
3. One cycle with a 22 hour hold at peak temperature
4. Two cycles with a 25 hour hold at peak temperature
5. One cycle with a 200 hour hold at peak temperature
6. One cycle with a 200 hour hold at peak temperature

Specimen lengths were recorded initially and at sufficiently long intervals to identify any trends in dimensional changes that might occur. Cycling was continued after trends were identified until the data indicated dimensional stability at the new length.

The effect of long term cycling at 1000°C (1832°F) on honeycomb specimens of GE-3202 and Corning 9460 is shown in Figure 21. This illustration also includes data for GE-7808 (frit base) honeycomb and monolithic specimens cycled at 1200°C (2192°F). The unusual behavior of GE-7808 honeycomb prompted inclusion of the data for the monolithic specimens. Examination of Figure 21 shows essentially no difference in the stability of GE-3202 and Corning 9460 during long term cycling, except that one expands and the other shrinks.

Short term dynamic cycling at 1150°C (2102°F) and at 1100°C (2012°F) has little effect on the dimensional stability of GE-7808 (frit and mineral base) honeycomb specimens after about 650 cycles. These data appear in Figure 22 which shows that both kinds of GE-7808 material have equal or slightly better dimensional stability than Corning 9460.

The effect of short term dynamic cycling on the dimensional stability of GE-3202 and Corning 9460 cycled at 1000°C (1832°F) is illustrated in Figure 23. These data indicate that the stability of GE-3202 is unaffected by variations in original firing temperature but the dimensional change of Corning 9460 is about half that of GE-3202.

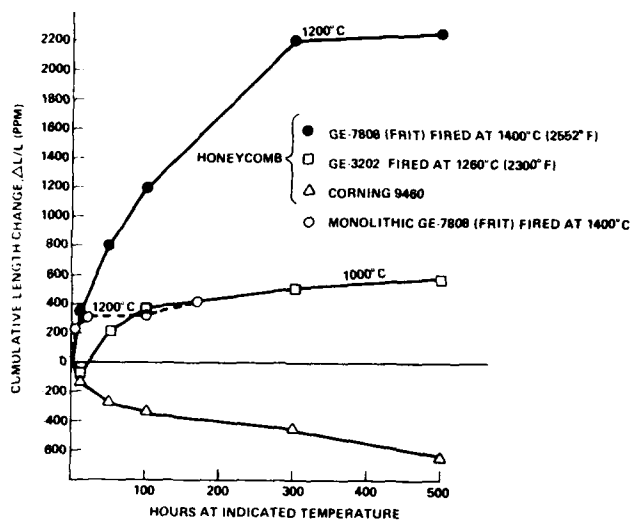


Figure 21. Effect of Long Term Thermal Exposure on Dimensional Stability of Honeycomb and Monolithic Materials

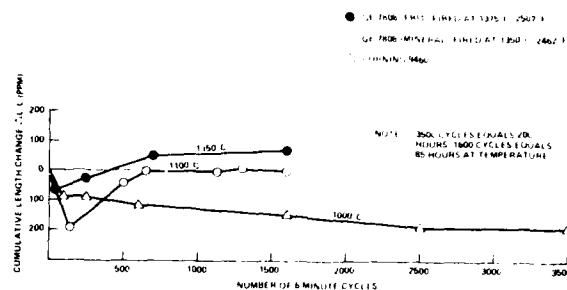


Figure 22. Effect of Thermal Cycling on Dimensional Stability of GE-7808

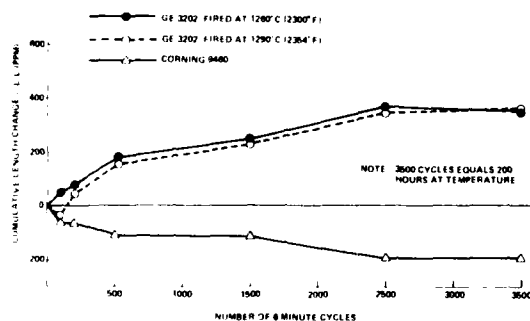


Figure 23. Effect of Thermal Cycling on Dimensional Stability of GE-3202

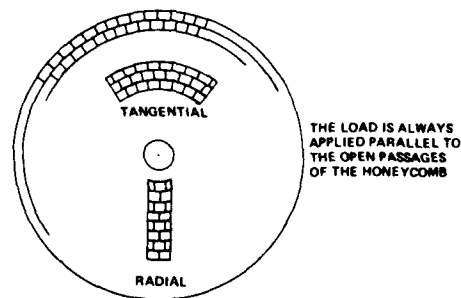


Figure 24. Orientation of Mechanical Test Specimens Cut from a Cylindrical Honeycomb Structure

### 5.7 Mechanical Properties

Monolithic specimens 6 mm x 6 mm x 51 mm (0.25" x 0.25" x 2.0"), ground flat to a tolerance of  $\pm 0.025$  mm ( $\pm 0.001$  in.), were subjected to four-point flexure using a 6 mm x 51 mm surface as the tensile surface. The outer knife edge span was 38.1 mm (1.5") and the inside span was 12.7 mm (0.5"). A cross-head speed of 0.51 mm/min. (0.002 in/min) was used for all tests.

Modulus of rupture (MOR) and elastic modulus (MOE) data were obtained on honeycomb specimens of the following geometry: 88 mm (3.5") long, 12.7 mm (0.5") thick, and 19 mm (0.75 inch) wide. Specimen surfaces were ground to a tolerance of  $\pm 0.51$  mm ( $\pm 0.02$ ") on all dimensions and loads were applied in four point flexure using a 19 mm x 88 mm surface as the tensile surface. The outer knife edge span was 62 mm (2.5") and the inside span was 19 mm (0.75"). Open passages of the honeycomb were perpendicular to the tensile surface and specimens were tested in both the tangential and radial orientations. Figure 24 is a schematic illustration of specimen orientation. A load application rate of 1380 kPA/minute (200 psi/minute) was used for both kinds of specimen.

The mechanical properties of the materials investigated, summarized in Table 2 show that the GE honeycomb materials are consistently stronger in the tangential direction, but with the exception of GE-7808 (frit base) material are weaker in the radial direction. These data also reveal that the GE materials, except the mineral version of GE-7808, are about equal in strain tolerance to Corning 9460. Strain tolerance is the ratio,  $MOR/MOE \times 10^6$ , and indicates the ability of a regenerator core to survive the large tangential tensile stress at the hot face outside diameter. The low value exhibited by the mineral version of GE-7808 probably reflects the slightly high porosity of this material, which can be overcome through additional processing development.

### 5.8 Ford Motor Company Tests

Additional laboratory screening tests of the mineral based GE-7808 for sodium resistance were conducted at the Ford Motor Company laboratories in Dearborn, Michigan. The procedures for sample preparation, testing, and evaluation are as follows:

Standard laboratory specimens, nominally 25.4 mm x 25.4 x 76.2 mm (1 inch x 1 inch x 3 inch) rectangular parallelepipeds were cut from bulk matrix honeycomb with the major dimension in the axial direction. The axial faces were ground flat and parallel to each other to within 0.025 mm (0.001 inch). The samples were then degreased by a five-minute ultrasonic treatment in ACS acetone. A five minute ultrasonic cleaning in distilled water was then carried out, and the excess water was blown out of the honeycomb samples using filtered compressed air. The samples were dried at 200°C (392°F) and fired to 500°C (932°F) to complete the cleaning procedure. Initial length measurements of the cleaned samples were determined using a Sheffield Visual Comparator with 5000:1 amplification. The lengths are measured to the nearest  $2.5 \times 10^{-5}$  mm (one millionth of an inch) and the measurement is reported to be accurate to  $\pm 1.3 \times 10^{-4}$  mm ( $\pm 5$  millionths of an inch).



The hot face chemical attack test provides a source of sodium ions for exchange with a host lattice cation by soaking the material in a 3.5% sodium chloride solution. The treated specimen is air dried for two hours at 200°C (392°F), fired at 800°C (1472°F), and stability (change in length) measurements are periodically carried out. The change in the material's thermal expansion behavior between room temperature and 1100°C (1982°F) is also determined, as a significant change in this material characteristic is an indication of material instability.

### 5.9 Microstructure and Related Properties

The microstructure of a material depends primarily on the kinds and amounts of phases, including pores, which are present. To some extent, the properties of a material are influenced by the microstructure, but the external configuration can also be a factor. Consequently, the properties of so unique a structure as a honeycomb can be significantly affected by both of these conditions.

One of the properties which received considerable attention during the materials development phase of this program was density. This property is, of course, highly dependent on the particle size and distribution of the starting materials, the fabrication method, and the time and temperature of the firing cycle.

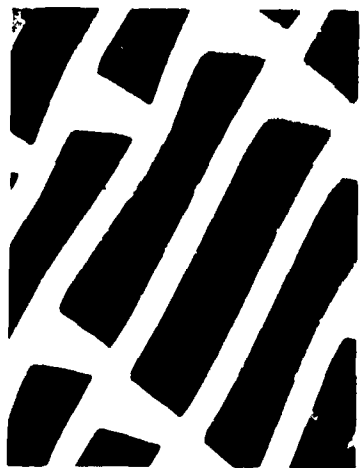
Some care was taken to fabricate the monolithic test bars in a manner that would produce comparable density, in each composition, to the density obtained in honeycomb cores fabricated at Coors when fired at the same temperature. This was generally successful as shown in the following data for open porosity. An apparent exception can be noted in the case of the GE-7808 frit based material, however, the difference in firing conditions is believed to be the major cause of the difference in open porosity. Note that the density values for the honeycomb include the effect of the very open cellular structure of the honeycomb.

Monolithic	Density g/cc	Open Porosity %	Firing Cycle
GE-3202	2.27	3.7	1260°C/3 hrs.
GE-7808 (frit)	2.53	0.3	1400°C/4 hrs.
GE-7808	2.12	10.2	1400°C/4 hrs.
Honeycomb			
GE-3202	0.79	7.0	1260°C/9.3 hrs.
GE-7808 (frit)	0.96	8.8	1375°C/4 hrs.
GE-7808 (mineral)	0.94	9.2	1380°C/4 hrs.

Pore size was measured by mercury porosimetry on the honeycomb materials and was determined as 1.70, 2.40, and 4.45 microns for GE-7808 (mineral), GE-7808 (frit) and GE-3202, respectively.

Variations in honeycomb cell geometry associated with different fabrication processes are shown in Figures 25a through 28a. The refractory nature of GE-7808 material is evident by very little cell distortion although the material was fired at 1400<sup>0</sup> C (2552<sup>0</sup> F). The triangular geometry reportedly<sup>(2)</sup> provides the best combination of heat transfer and flow friction characteristics. The specimen shown in Figure 28 was fabricated by NGK Insulators, Ltd., using the extrusion process.

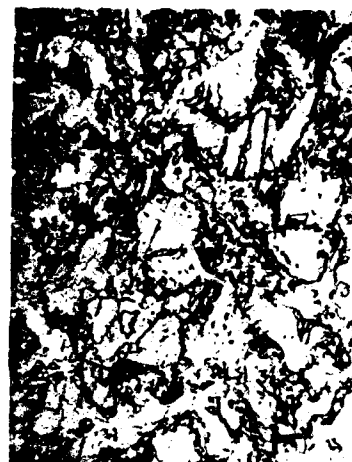
Microstructural examination of GE-3200, GE-3202, GE-7808 (frit base) and Corning 9460 was conducted using standard ceramographic techniques for specimen preparation. The photomicrographs, Figures 25b through 28b, show the inherent porosity of honeycomb structures and reveal the smaller grain size of Corning 9460 compared to the General Electric Company materials. However, the beneficial rheological behavior of the multi-phase General Electric Company materials appears to maintain the honeycomb channels more nearly parallel to the axis of the regenerator core than do some of the single phase (glass ceramic) materials.



26X

CELLS ARE ABOUT 0.5 mm x 2.5 mm  
(0.02" x 0.1").  
CELL WALLS ARE ABOUT 0.2 mm  
(0.008").

(a)

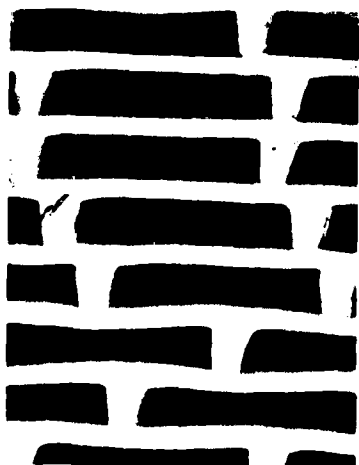


1000X

LARGER PARTICLES ARE ABOUT  
20 MICRONS.

(b)

Figure 25. Macro and Micro Structure of GE-3202 Honeycomb Material Fabricated by the Calendering Process and Fired at 1260°C (2300°F)



21X

CELLS ARE ABOUT 0.5 mm x 2.5 mm  
(0.02" x 0.1").  
CELL WALLS ARE ABOUT 0.2 mm  
(0.008")

(a)

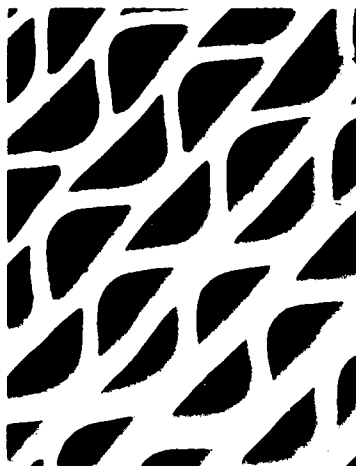


1000X

LARGER PARTICLES AVERAGE ABOUT  
12 MICRONS.

(b)

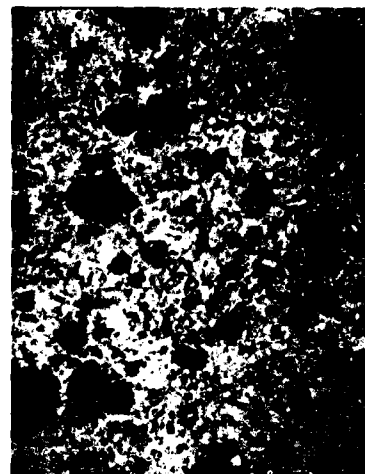
Figure 26. Macro and Micro Structure of GE-7808 Frit Base Material Fabricated by the Calendering Process and Fired at 1400°C (2552°F)



21X

CELL WALLS ARE ABOUT 0.13 mm  
(0.005").

(a)

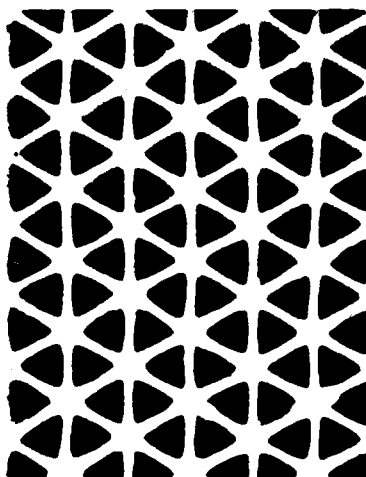


1000X

PARTICLE SIZE AVERAGES ABOUT  
7 MICRONS.

(b)

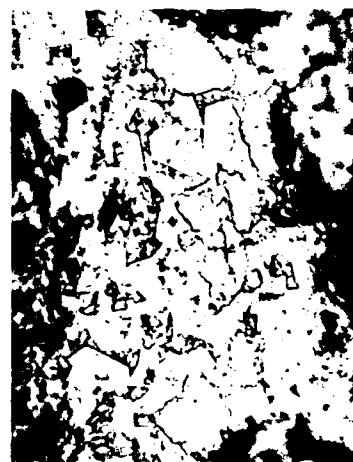
Figure 27. Macro and Micro Structure of Corning 9460  
Fabricated by the Coated Paper Wrapping Process



12X

CELL WALLS ARE ABOUT 0.2 mm  
(0.0008").

(a)



1000X

LARGER PARTICLES ARE ABOUT  
20 MICRONS.

(b)

Figure 28. Macro and Micro Structure of GE-3200 Honeycomb Material  
Fabricated by the Extrusion Process and Fired at 1200°C (2192°F)  
by NGK, Nagoya, Japan

## 6. DISCUSSION OF RESULTS

Although the preceding section included brief discussions of some of the results, this section concentrates on a few of those factors which greatly influence dimensional stability and performance. Therefore, a more detailed description is presented on corrosion resistance, thermal cycling, microstructural changes, and mechanical properties.

When petalite ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$ ) and spondumene ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ) are calcined above  $900^\circ\text{C}$  ( $1652^\circ\text{F}$ ) the resultant beta forms of these LAS materials exhibit very low thermal expansion. This property was a deciding factor in the selection of these materials as candidates for the early work in this program. However, the relative ease with which the  $\text{Li}^+$  atom can be removed chemically from the LAS structure guided our original work to an LAS/MAS mixed phase approach. We reasoned that low expansion would be provided by the LAS phase, while the MAS phase would contribute good corrosion resistance. This theory was substantiated by corrosion data which showed that the LAS/MAS materials, GE-3200 and GE-3202, were more resistant to acid and salt attack than was the original reference material Corning 9455, and LAS glass ceramic. However, the current reference material, Corning 9460, contains no lithium and exhibits considerably better corrosion resistance than both of the LAS/MAS and the LAS materials. The obvious implication that lithium is detrimental to corrosion resistance coupled with a mid-program requirement for greater refractoriness led to the investigation of a series of zirconia-modified MAS materials which resulted in the development of the GE-7808 (ZrMAS) composition. The excellent corrosion resistance of GE-7808, frit and mineral base, materials is related to their cordierite and zirconia contents and to the absence of large amounts of alkali oxides. Except for very small ( $< 1\%$ ) amounts of sodium and potassium oxides, none of the starting materials contains any readily leachable constituents.

The dimensional instability exhibited by GE-7808 frit base honeycomb during long term thermal exposure to  $1200^\circ\text{C}$  ( $2192^\circ\text{F}$ ) was not observed when the same material was dynamically cycled at  $1150^\circ\text{C}$  ( $2102^\circ\text{F}$ ). In fact, GE-7808 frit and mineral base, the latter cycled at  $1100^\circ\text{C}$  ( $2012^\circ\text{F}$ ), exhibit better dimensional stability after 600 six minute cycles than Corning 9460. However, in an attempt to explain this behavior, XRD analyses were repeated on the frit base GE-7808 and on specimens of cordierite (MAS) frit. Both monolithic and powder specimens were used to negate the possible influence of micro-structural orientation. Although this effect was not observed, XRD patterns of the MAS frit contained some small, unidentified peaks. A thin section of the MAS material was prepared and examined both optically and with a Cameca MS 64 electron probe X-ray microanalyzer. Optical examination of  $1000\times$  with transmitted light revealed a crystalline phase within the MAS grains. Microprobe analysis of these inclusions indicated areas rich in Ba, Al, and Si but poor in Mg. Review of the ASTM data file suggested the included phase was celsian,  $\text{BaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . A search of the literature revealed that celsian<sup>(5)</sup> has a reversible alpha-to-beta transformation at  $300^\circ\text{C}$  ( $572^\circ\text{F}$ ) which is accompanied by a large, rapid volume change and expands almost  $1\%$  between  $25^\circ\text{C}$  and  $1000^\circ\text{C}$  ( $77^\circ\text{F}$  -  $1832^\circ\text{F}$ ). Some celsian was synthesized, a test bar was made and measurement of its thermal expansion confirmed the information from Reference 5 as shown by our data in Figure 29. These results clearly show that large amounts of celsian could detrimentally influence dimensional stability.

Further evidence of the excellent dimensional stability of GE-7808 frit and mineral base materials is revealed by their resistance to both alkali and acid attack. Both GE-7808 and Corning 9460 are about equally resistant to acid attack, but the GE materials are significantly more resistant to alkali attack than the reference material.

The elastic modulus (MOE) and modulus of rupture (MOR) of a honeycomb structure are related to the geometry of the structure. Of course, other factors such as degree of bonding of the structure, microstructure of the material, and intrinsic materials properties can be influential. Since strain tolerance is the ratio of MOR/MOE, this parameter is influenced by the same factors. The effect of fabrication on microstructure is well known and its effect on the degree of bonding at each cell structure during honeycomb formation must also be important. It is this combination of parameters, we believe, which accounts for the strength differences between radially and tangentially oriented General Electric Company materials and the Corning reference materials. However, because the critical thermal stress in a regenerator core is the tangential tension at the periphery of the hot face, the strain tolerance in the tangential direction is a more important parameter than the radial strain tolerance, and is more critically assessed by design engineers.

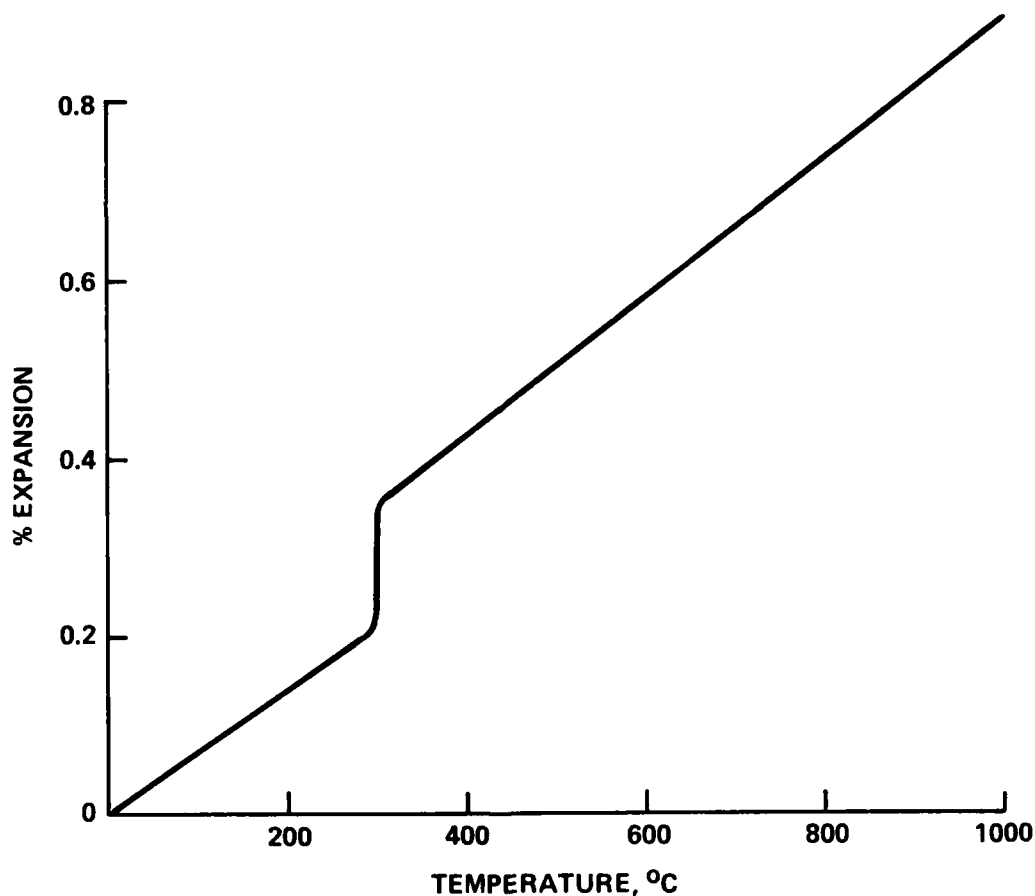


Figure 29. Thermal Expansion Behavior of Celsian

## 7. COST STUDY

Based on information obtained from various materials suppliers and from a Ford Motor Company manufacturing cost study<sup>(6)</sup>, the cost of the ceramic material alone for preheater cores made of GE-7808 (mineral base) was estimated at \$1.52/core in quantities of 500,000 cores/year. (By comparison, the Ford study includes a cost of \$11.00 for the MAS frit portion in their estimate of cores priced at \$38-46 each.) Estimated costs of \$28.50 to 36.50/core for mineral base GE-7808 are based on the following assumptions and calculations:

1. All costs other than the ceramic material costs are assumed to be the same as in the 1977 Ford estimates. Thus, the estimated total costs of \$28.50 to \$36.50 per core are simply based on reducing the material costs by \$9.50 per core as indicated above.
2. A finished size core of 368.3 mm (14.5 in) O.D. x 25.4 mm (1.0 in) I.D. x 88.9 mm (3.5 in) thick weighing 20 pounds was chosen for the study.
3. Based on the use of cordierite frit at 50 ¢/lb and allowing 10% excess for scrap or other processing losses, \$11.00 was used as the original ceramic raw material cost. (This price of cordierite frit has markedly increased since the inception of this program.)
4. The mineral based GE-7808 costs include raw material as well as costs for separately, lightly (1000°C) calcining the clay and talc used to form the cordierite at their respective sources in order to remove the approximately 13% loss on ignition associated with these materials while at the same time reducing the eventual firing shrinkage of the final product cores. If it proves necessary to first mix these two ingredients before calcining in order to promote cordierite formation, an additional freight charge of \$10,000/yr or about \$0.01/core unit may be necessary to cover the costs of bringing these raw materials together before calcining. Calcining and freight rates were provided by suppliers as \$17.50/ton and \$36/ton respectively and we have added on 10% loss factor in estimating the  $11 \times 10^6$  lbs/yr needed to make 500,000, 20 lb cores.

## 8. CONCLUSIONS

A multi-phase, frit base material consisting of zirconia-modified cordierite (ZrMAS) which is dimensionally stable up to 1150°C (2102°F), has excellent corrosion resistance, and expands less than 3000 ppm at 1000°C (1832°F) has been developed. This material has been designated GE-7808.

A mineral base version of GE-7808 was demonstrated late in the program using a lightly calcined clay/talc mixture to supply the cordierite (MAS) phase. This material represents a significant economic improvement over the frit base material, but further work is required to optimize its mechanical and thermal properties.

The rheological behavior of both the frit and mineral base GE-7808 materials combined with their chemical, microstructural, thermal, and mechanical properties indicate that this material has potential for use in rotary regenerative heat exchangers in automotive gas turbine engines.



## 9. REFERENCES

1. Grossman, D.G. and Lanning, J.G., "Aluminous Keatite Ceramic Regenerators," *Bull. Am. Ceram. Soc.* 56 (5) 474-77 (1977)
2. Cook, J.A., et al, "Evaluation of Advanced Regenerator Systems," NASA CR-159422, Ford Motor Company, August 1978
3. Rauch, H.W., Sr., "Improved Ceramic Heat Exchanger Material," NASA CR-135292, General Electric Company, November 1977
4. Nielsen, T.H., "Fabrication of Rectangular Cell Ceramic Regenerators for Use in Gas Turbine Engines," Paper No. 77-GT-111, presented at the ASME Gas Turbine Conference and Products Show, Philadelphia, PA, March 27-31, 1977
5. Yoshiki, B. and Matsumoto, K., "High-Temperature Modification of Barium Feldspar," *J. Am. Ceram. Soc.* 34 (9) 283-6 (1951)
6. Fucianari, C.A., et al, "Ceramic Regenerator Systems Development Program," NASA CR-159541 Ford Motor Company, March 1979
7. Fucinari, C.A., et al, "Ceramic Regenerator Systems Development Program," NASA CR-165139, Ford Motor Company, October 1980

